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(54) **A water-swellaible particulate absorbent material and method for producing this material.**

(57) Water-swellaible particulate absorbents have improved dispersibility in blood by surface-treatment with a hydrocarbon compound which is an aliphatic hydrocarbon or a substantially nonionic derivative thereof which is non-volatile and has a melting point below 35°C, or is a C<sub>12</sub>-C<sub>18</sub> alkyl trimethylammonium halide. Examples of suitable aliphatic hydrocarbons are n-dodecane, n-hexadecane; n-heptadecane and n-octadecane. Preferred derivatives are fatty alcohols, fatty acids and fatty acid esters.

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see front page

ABSORBENT MATERIALS

This invention relates to absorbent materials, more especially absorbent materials suitable for use in absorbent disposable products such as sanitary towels or napkins and tampons and absorbent products for surgical or medical use.

5 The invention also relates to processes for producing such materials and to absorbent articles containing such materials.

In recent years there has been much interest in the synthesis of absorbent polymers having a high capacity for absorbing water and body fluids. A number of different  
10 polymers have been developed some being wholly synthetic in nature and some partially synthetic.

Among the partially synthetic absorbent polymers are those based on starch. These include the starch-acrylonitrile graft copolymers described in US Patent Specifications Nos. 3,997,484 (the USA as represented by the Secretary of Agriculture) and 3,661,815 (Grain Processing Corporation), and the cross-linked gelatinised starch derivatives described in German Patent Application No. 2702781. Other examples of partially synthetic absorbent polymers are the carboxymethylated cellulose described in US Patent Specification No. 3,589,364 (Buckeye Cellulose Corporation), and the carboxymethyl-cellulose cross-linked by acid inter-esterification as described by Podlas, T.J., in INDA Tech. Symp. 1976, 2-3 March, pp 25-39.

Wholly synthetic absorbents include polyacrylates cross-linked with a polyamide/epichlorhydrin material as described in US Patent Specification No. 4,076,673 (Dow Chemical Company) and the potassium salts of polyacrylic acid cross-linked by aluminium ions as described in US Patent Specification No. 4,090,013 (National Starch and Chemical Corporation).

The above materials are substantially water-insoluble and absorb many times their weight of water, urine or other aqueous body exudates. They retain a particulate character as they imbibe surrounding liquid and swell. In most cases, even with water, the swollen particles are gelatinous and tacky and form clusters. An exception is the cross-linked

starch derivative described in German Patent Application No.2702781, the particles of which on absorbing water are substantially non-tacky and dry to the touch. However, even this starch derivative, as well as the other absorbents previously referred to, has poor dispersibility in blood, 5 that when blood is brought into contact with a mass of the absorbent significant penetration into the bed and hence absorption is extremely slow. The particles have therefore what may be described as poor "blood wet-out" so that on 10 exposure to blood the particulate material at the inside of a mass remains unreached by the blood. Although the mechanism is not understood at the present time, it appears that the blood on initial contact with the particles forms some sort of mass which acts as a barrier to the passage of 15 the blood through the surface layers of the particles.

An object of the invention is to provide an absorbent composition having improved blood dispersibility, or "blood wet-out". It is also an object to provide a process for producing such an improved absorbent.

20 According to the invention there is provided a water-swellaable particulate absorbent material surface-treated to enhance its dispersibility in blood with a hydrocarbon compound which is an aliphatic hydrocarbon or a substantially nonionic derivative thereof, which aliphatic hydrocarbon or 25 nonionic derivative is non-volatile and has a melting point below 35°C, or is a C<sub>12</sub>-C<sub>18</sub> alkyl trimethylammonium halide. the amount of the hydrocarbon compound being such as to

permit capillary flow of blood through a mass of the particulate absorbent.

The aliphatic hydrocarbon or nonionic derivative preferably has a melting point below about  $30^{\circ}\text{C}$ , and more preferably is liquid at room temperature. The most preferred hydrocarbons and nonionic derivatives are those which have melting points below about  $20^{\circ}\text{C}$ .

By non-volatile we mean that the aliphatic hydrocarbon or nonionic derivative thereof has a boiling point of at least  $150^{\circ}\text{C}$ , preferably at least  $200^{\circ}\text{C}$ . Treatment with the non-volatile compounds gives a longer lasting benefit than would be given by volatile compounds.

Examples of suitable aliphatic hydrocarbons are n-dodecane, n-hexadecane, n-heptadecane and n-octadecane. Preferred nonionic derivatives of aliphatic saturated or unsaturated hydrocarbons are fatty alcohols, fatty acids and fatty acid esters. Examples of fatty alcohols are nonan-1-ol, decan-1-ol, undecan-1-ol and dodecan-1-ol. Examples of suitable fatty acids which may be used are n-hexanoic acid, n-octanoic acid, n-nonanoic acid, 9-octadecenoic acid, 9,12-octadecadienoic acid and 9,12,15-octadecatrienoic acid; these fatty acids are substantially nonionic in character, exhibiting very low dissociation constants. Examples of suitable fatty acid esters are the glycerides constituting the edible oils, soybean oil, cottonseed oil, corn oil, peanut oil, safflower oil, sunflower oil, olive oil, rapeseed oil, coconut oil and palm

kernel oil. Other examples of suitable fatty acid esters are the fatty acid esters of sorbitol and poly(ethylene oxide) condensates thereof such as sorbitan mono-oleate (available commercially under the trade name SPAN 80) and  
5 polyoxyethylene (20) sorbitan monostearate (available commercially under the trade name TWEEN 60). However, esters of other polyhydric alcohols may be used. The ester is desirably substantially odourless.

Those aliphatic hydrocarbons and nonionic derivatives  
10 thereof which are solid at room temperature (say 22°C) exert their beneficial effect under conditions at which they are liquid and therefore absorbents treated with such compounds are required to be used under conditions where the temperature will exceed their melting point, for  
15 example in a menstrual tampon.

The C<sub>12</sub>-C<sub>18</sub> alkyl trimethylammonium halide may, for example, be cetyl trimethylammonium bromide or chloride.

The hydrocarbon compound used for the treatment of the absorbent material should of course be inert and physio-  
20 logically acceptable.

The water-swellable absorbent materials which may be treated with the hydrocarbon compound are exemplified by the partially synthetic and wholly synthetic absorbent polymers described above. The water-retention values of  
25 such polymers are at least 2 g/g and are usually much higher. The particulate absorbent material may be in the form of a powder, granules, flakes or fibres.

The treatment of the absorbent with a liquid hydrocarbon compound may be effected simply by directly mixing the particulate absorbent with the hydrocarbon compound. When a hydrocarbon compound is used which is solid at normal  
5 temperature it is necessary to first melt the hydrocarbon compound and then to thoroughly mix the particulate absorbent with the molten compound. Mixtures of solid and liquid hydrocarbon compounds would also require to be heated to melt the solid component.

10 The treatment of the absorbent with the hydrocarbon compound may be effected by first dissolving the hydrocarbon compound in a suitable volatile solvent and after thoroughly mixing the absorbent with this solution, heating the mixture to drive off the solvent. Solvents which may be used are  
15 the lower aliphatic alcohols, preferably ethanol or isopropanol, although any other solvent could be used which is sufficiently volatile to permit its ready removal after admixture with the absorbent material. It may be possible to produce the surface-treated absorbent by adding the hydro-  
20 carbon compound in solution in a solvent during the process of manufacturing the absorbent. For example, in the case of the absorbent described in German Patent Application No. 2702781, the starch derivative in its acid form is conveniently mixed with a solution of the hydrocarbon compound in a  
25 volatile solvent and an alkali, eg sodium carbonate or ammonium hydroxide, and the mixture heated to obtain as a dry powder the treated starch derivative in the salt form.

The amount of the hydrocarbon compound that is used for the treatment of the absorbent depends on a number of factors. The amount which is sufficient to effect the enhancement of the dispersibility of the absorbent in blood (ie the "blood wet-out" of the absorbent) may vary with the chemical type of absorbent and its physical form, eg particle size, and the hydrocarbon compound used in the treatment, as well as on the method of treatment. It should be noted, however, that excessive amounts of the hydrocarbon compound inhibit blood dispersibility by preventing capillary flow of blood through a mass of the particulate absorbent. It is required that the blood should be able to percolate through the capillaries or spaces between the particles and therefore these should not be blocked by the hydrocarbon compound. If this occurs the blood would be forced to travel through the mass by diffusion alone: this is a relatively slow process and corresponds to very poor blood wet-out properties. Consequently, the amount of the hydrocarbon compound used for the treatment of the absorbent should not be such as to result in, for example, a mixture having a paste-like or ointment-like consistency such as is produced by the composition described in Example 6 of British Patent Specification No.1,454,055 (Pharmacia AB).

Employing the gelatinised starch derivatives described in German Patent Application No.2702781 good results have been



obtained using as little as 1-5% by weight of a liquid aliphatic hydrocarbon or solid  $C_{12}-C_{18}$  alkyl trimethylammonium halide based on the weight of absorbent. The edible oils are generally required to be used in greater amounts than the liquid aliphatic hydrocarbons. For most absorbent materials the amount of hydrocarbon compound will not normally be required to exceed about 30% by weight of the absorbent polymer.

By treatment of an absorbent with a hydrocarbon compound in accordance with the invention one can also improve the feel to the touch of a mass of absorbent swollen with blood. Many absorbent polymers become very sticky to the touch when blood is added to a mass of the particles. We have found that treatment with the hydrocarbon compound reduces this stickiness.

The treatments described do not markedly affect the blood retention value of an absorbent.

The invention also relates to liquid absorbent articles containing the absorbent material of the invention. The liquid absorbent article may comprise a fibrous carrier or support for the absorbent material, such as a woven or unwoven material such as cotton cloth, rayon, wool, surgical gauze or paper as well as cellulosic fluff, on or within which the absorbent material is supported. The absorbent material may be spread on the carrier or it may be mixed with loose fibres to make a composite fluff or wadding which can be enclosed between cover sheets of paper or cloth.

The article may also be in the form of a laminate. In a particular form, the carrier comprises two sheets between which the absorbent material is sandwiched. The absorbent materials of the invention are particularly suitable for use in sanitary towels, napkins or tampons. The production of an absorbent article utilising a particulate absorbent material is described for example in German Patent Application No.2702781.

The invention will now be illustrated by the following Examples. Percentages are by weight.

References herein to the "dry-off" of an absorbent refer to feel of the polymer to the touch after a mass of particles of the absorbent has absorbed blood. An absorbent with poor dry-off would be sticky to the touch whereas one with a good dry-off would feel substantially dry and non-sticky. Water and urine retention values are given to the nearest quarter of a unit. They were determined by the procedure described in German Patent Application No.2702781.

Examples 1 to 9

Potato starch (1,000 g) was slurried in water (950 ml) containing epichlorhydrin (8.4 ml; 1.0% epichlorhydrin by weight of starch). Sodium hydroxide (5 g) in water (50 ml) was added with stirring and the mixture was applied to a heated roller via a feeder roller to form a layer on the surface of the roller of about 0.5 mm thickness. The roller itself was heated using steam at 3.77 bars (140°C).

The cross-linked starch derivative was removed from the roller as a flake material to yield 914 g of product. The soluble content of the product was found to be 25.0 mg/g and the product was found to have a bed volume of 13.5 ml/g.

- 5 Since about half of the epichlorhydrin was lost by evaporation from the heated roller the degree of substitution of the cross-linking groups was about 0.01.

- 10 Sodium hydroxide (34 g) in water (66 ml) followed by monochloroacetic acid (39 g) in water (11 ml) was slowly added with stirring to the cross-linked potato starch (100 g) as prepared above. The mixture was aged overnight in a polythene bag. The theoretical degree of substitution was 0.67.

- 15 The moist carboxymethyl derivative was dispersed in 10 times its weight of 1N hydrochloric acid and soaked for 15 minutes and then filtered. The gel cake was repeatedly dispersed in water and filtered until the filtrate was substantially free of chloride ions. Ammonium hydroxide, specific gravity 0.910 (70 ml) was mixed with the water-  
20 swollen washed cake before drying in a forced air oven (70°C) and milling (2 mm screen). The milled product had a water retention value of 20.00 g/g, a urine retention value of 10.25 g/g, a solubility of 0.3% and a bed volume of 51 ml/g.

- 25 Various liquid hydrocarbon and hydrocarbon derivatives were used to treat the control material prepared as described above by thoroughly mixing them with the absorbent. The

percentages of the hydrocarbons and hydrocarbon derivatives added which are given in Table I are based on the weight of the control material. In each case the treated absorbent was of particulate form.

5

Table I

| <u>Example</u> | <u>Additive</u>                                       | <u>% Added</u> |
|----------------|---|----------------|
| 1              | n-dodecane  | 1              |
| 2              | n-hexadecane  | 1              |
| 3              | decan-1-ol  | 5              |
| 10 4           | n-nonanoic acid                                       | 10             |
| 5              | Olive oil   | 5              |
| 6              | Soybean oil   | 5              |
| 7              | Peanut oil  | 5              |
| 8              | Sorbitan mono-oleate (SPAN 80)                        | 5              |
| 15 9           | Polyoxyethylene (20) sorbitan monostearate (TWEEN 60) | 5              |

The products of Examples 1 to 9 showed a marked improvement in blood wet-out and dry-off compared to the control material to which no addition had been made.

The ability of an absorbent to be wet-out by blood was assessed by placing 1-2 g of the absorbent to be treated on a watch glass and adding to it 1-3 ml of blood. In the cases where the absorbent had been treated with a hydrocarbon or hydrocarbon derivative the blood rapidly penetrated the mass of particles whereas in the case of the control material the blood only very slowly, if at all, penetrated the mass to reach the particles in the interior

of the mass. All blood wet-out testing was carried out at room temperature (about 22°C).

Examples 10 to 12

The hydrocarbon n-dodecane was added directly, with thorough mixing, to the absorbent materials as described in Table II, each of which had a water retention value greater than 2 g/g. In each case the blood wet-out and dry-off of the absorbent was improved compared to the respective unmodified absorbent.

10

Table II

| <u>Example</u> | <u>Absorbent</u> | <u>% n-dodecane</u> |
|----------------|------------------|---------------------|
| 10             | Absorbent A      | 10                  |
| 11             | Absorbent B      | 10                  |
| 12             | Absorbent C      | 2                   |

15

Absorbent A was the potassium salt of a polyacrylic acid cross-linked by aluminium ions available commercially from National Starch Corporation under the trade name Permasorb and generally described in US Patent Specification No.4,090,013.

20

Absorbent B was a carboxymethylated cellulose cross-linked by intermolecular esterification and available from Hercules Corporation under the trade name SPX 1154 and generally described by Podlas, T.J., in INDA Tech. Symp. 1976, 2-3 March, pp 25-39. It is a particulate fibrous material.

25

Absorbent C was a starch-polyacrylonitrile graft copolymer prepared in accordance with the process described in US Patent No. 3,981,100.

Examples 13 to 16

5       Cetyl trimethylammonium bromide (CTAB), dissolved in a small volume of absolute ethanol, was thoroughly mixed with the absorbent materials indicated in Table III, each of which had a water retention value greater than 2 g/g. The mixtures were placed in a forced air oven at 60°C to  
10   remove the solvent. The amount of cetyl trimethylammonium bromide given in Table III is based on the weight of the control material. In each case the blood wet-out and dry-off of the treated material was improved compared to the control material to which no addition had been made.

15

Table III

| <u>Example</u> | <u>Absorbent</u> | <u>% CTAB</u> |
|----------------|------------------|---------------|
| 13             | of Example 1     | 5             |
| 14             | Absorbent A      | 20            |
| 15             | Absorbent D      | 20            |
| 20   16        | Absorbent E      | 30            |

Absorbent D was a hydrolysed starch-polyacrylonitrile graft copolymer available from the Grain Processing Corporation under the trade name Polymer 35-A-100 and generally described in US Patent No. 3,661,815.

25       Absorbent E was a hydrolysed starch-polyacrylonitrile graft copolymer available from General Mills Inc., under

the trade name SGP-502S and generally described in US  
Patent No. 3,997,484.

In co-pending application No. 78300507.7 there is  
described another means of enhancing the dispersibility in  
5 blood of a water-swellaable particulate absorbent material,  
wherein the absorbent material is surface-treated with  
one or more polyethers containing oxyethylene and/or  
oxypropylene groups.

CLAIMS:

1. A water-swellaable particulate absorbent material, characterised in that it is surface-treated to enhance its dispersibility in blood with a hydrocarbon compound which is an aliphatic hydrocarbon or a substantially nonionic derivative thereof, which aliphatic hydrocarbon or nonionic derivative is non-volatile and has a melting point below 35°C, or is a C<sub>12</sub>-C<sub>18</sub> alkyl trimethyl-ammonium halide, the amount of the hydrocarbon compound being such as to permit capillary flow of blood through a mass of the particulate absorbent.
2. An absorbent material as claimed in Claim 1, characterised in that the aliphatic hydrocarbon derivative is a fatty alcohol, fatty acid or fatty acid ester.
3. An absorbent material as claimed in Claim 1 or Claim 2, characterised in that the aliphatic hydrocarbon or nonionic derivative thereof is a liquid.
4. An absorbent material as claimed in any of Claims 1 to 3, characterised in that the hydrocarbon compound is an edible oil.
5. An absorbent material as claimed in any of Claims 1 to 4, characterised in that the absorbent is treated with an amount of the hydrocarbon compound of from 1 to 30% by weight of the untreated absorbent.
6. A method of producing a water-swellaable particulate absorbent material as claimed in Claim 1 having enhanced dispersibility in blood, characterised by contacting the absorbent material with one or more



hydrocarbon compounds as defined in Claim 1 to form a coating of hydrocarbon compound on the surface of the particles.

7. A method as claimed in Claim 6, characterised by intimately mixing water-swellaable particulate absorbent material with one or more liquid or liquefied hydrocarbon compounds as defined in Claim 1, the amount of hydrocarbon compound employed being such as to permit capillary flow of blood through a mass of the treated particulate absorbent.

8. A method as claimed in Claim 6, characterised by intimately mixing water-swellaable particulate absorbent material with a solution in a volatile solvent of one or more hydrocarbon compounds as defined in Claim 1 and then removing the solvent, the amount of hydrocarbon compound being such as to permit capillary flow of blood through a mass of the treated particulate absorbent.



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# EUROPEAN SEARCH REPORT

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Application number

EP 79 30 2110

| DOCUMENTS CONSIDERED TO BE RELEVANT                        |   |                   | CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)              |
|--|---|-------------------|---|
| Category   | Citation of document with indication, where appropriate, of relevant passages                   | Relevant to claim |   |
| X  | FR - A - 2 354 184 (DOW CHEMICAL)<br>* Page 1, lines 1-9, 36-40; page 5, lines 1-10; 35-39 *    | 1-8               | A 61 L 15/00  |
|  | --  |                   |   |
| X  | FR - A - 2 066 324 (D. TORR)<br>* Page 3, lines 33-40; page 4, lines 1-7; page 6, lines 18-26 * | 1-8               |   |
|  | --  |                   |   |
|  | US - A - 337 666 (A.W. LEWING)<br>* Column 6, lines 60-62; claims 1,21-23 *                     | 1-8               | TECHNICAL FIELDS SEARCHED (Int.Cl. 3)<br><br>A 61 L 15/00   |
|  | --  |                   |   |
|  | FR - A - 2 187 947 (F.M.C.)<br>* Page 2, lines 34-40; page 5, claims 1,3 *                      | 1-8               |   |
|  | --  |                   |   |
|  | US - A - 3 847 636 (F.R. SMITH)<br>* Column 3, lines 24-27; column 6, claim 1 *                 | 1-8               |   |
|  | --  |                   |   |
| A  | US - A - 2 602 042 (C.W. ABBOTT)  |                   | CATEGORY OF CITED DOCUMENTS                                 |
| A  | GB - A - 1 233 239 (RIEDEL TEXTILE)   |                   | X: particularly relevant                                    |
| A  | FR - A - 1 548 038 (PROCTER & GAMBLE)   |                   | A: technological background                                 |
| A  | FR - A - 1 134 126 (SANITARY PRODUCTS)  |                   | O: non-written disclosure                                   |
| A  | FR - A - 2 000 595 (KIMBERLEY-CLARK)  |                   | P: intermediate document                                    |
|  |   |                   | T: theory or principle underlying the invention             |
|  |   |                   | E: conflicting application                                  |
|  |   |                   | D: document cited in the application                        |
|  |   |                   | L: citation for other reasons                               |
| The present search report has been drawn up for all claims |   |                   | &: member of the same patent family, corresponding document |
| Place of search  | Date of completion of the search  | Examiner          |   |
| The Hague  | 10-01-1980  | PELTRE            |   |



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# EUROPEAN SEARCH REPORT

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EP 79 30 2110<sup>2</sup>

| DOCUMENTS CONSIDERED TO BE RELEVANT |   |                   | CLASSIFICATION OF THE APPLICATION (Int. Cl. 3) |
|-------------------------------------|---|-------------------|--|
| Category                            | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim |  |
| A                                   | <u>US - A - 4 055 184</u> (H. KARAMI)<br>-----                                |                   |  |
|                                     |   |                   | TECHNICAL FIELDS SEARCHED (Int. Cl. 3)         |
|                                     |   |                   |  |
|                                     |   |                   |  |